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Electronic excitation spectrum of thiophene studied by symmetry-adapted cluster configuration interaction method

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Electronic excitation spectrum of thiophene was investigated by the symmetry-adapted cluster (SAC)/SAC configuration interaction method. Seventy singlet and four lowest triplet electronic states of thiophene were computed to give a detailed satisfactory theoretical interpretation of the vacuum ultraviolet (VUV) spectrum and the electron energy loss spectrum of thiophene. The present calculations gave the $2\,^1A_1$ valence state at 5.41 eV and the $1\,^1B_2$ valence state at 5.72 eV with oscillator strengths 0.0911 and 0.1131, respectively, and the $5\,^1A_1$ valence state at 7.32 eV and the $4\,^1B_2$ valence state at 7.40 eV with oscillator strengths 0.3614 and 0.1204, respectively. These valence-excited states were assigned to the two strong absorption bands of the VUV spectrum centered around 5.5 and 7.05 eV, respectively. A number of Rydberg transitions were obtained and assigned to the 6.0, 6.6, and 7.5–8.7 eV, etc. energy regions. The similarities and differences in the electronic excitations between thiophene and other five-membered ring compounds were discussed. The accuracy and assignment of the present results are compared with those of the recent theoretical studies by CASPT2 and multireference double configuration interaction methods.
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I. INTRODUCTION

The electronic spectra of the five-membered ring compounds cyclopentadiene (CP), furan, and pyrrole have been the subjects of many experimental and theoretical studies.[1–37] The interest in these molecules is not surprising, considering that these molecules are fundamental units in many important biological molecules. Furthermore, their electronic excitation spectra have received much attention in recent years as benchmark examples for theoretical studies of excited states. The electronic excited states of CP, furan, and pyrrole have been successfully studied in our recent studies[38,39] using the symmetry-adapted cluster configuration interaction (SAC-CI) method that offers a consistent interpretation of the electronic excitation spectra of these molecules. As a series of this study, we examine here the excitation spectrum of thiophene. By a replacement of oxygen with sulfur, a second-row element, very interesting changes occur in both ground and excited states.

The electronic absorption spectrum of thiophene has been intensively investigated since the beginning of the last century. A comparison of condensed phase spectra[12–14] with gas phase data confirms the valence nature of the strong bands around 5.5 and 7.05 eV and suggests that the weak fine structure with onset around 6.0 eV is attributed to a Rydberg excited state. The magnetic circular dichroism (MCD) spectrum of thiophene[16–18] in solution of hexane shows two bands at 5.27 and 5.64 eV, respectively, having opposite signs in their *B*-values. Electron energy loss (EEL) spectra have been reported,[19–21] and they show that two lowest-lying triplet excited states (both $^3\pi-\pi^*$) were located at about 3.8 and 4.7 eV. These experimental data will be discussed in detail below in the light of the present theoretical calculations.

To the best of our knowledge, there have been two sophisticated *ab initio* studies on the excited states of thiophene. Bendazzoli *et al.*[12] obtained six lowest excited A_1 states (three for each of singlet and triplet), and eight lowest of each of the symmetries A_2, B_2, and B_1 by the configuration interaction (CI) method using a double-zeta basis set. In their study, two pairs of valence $\pi-\pi^*$ excited states were given in the order, $^1A_1(\text{middle})<^1B_2(\text{middle})<^1A_1(\text{strong})<^1B_2(\text{very strong})$. More extensive *ab initio* study was given by the CASPT2 (Ref. 29) method giving the same intensity order as Bendazzoli's, but only the $1a_2\rightarrow n=3$ and $3b_1\rightarrow n=3$ series of Rydberg states in the lower energy region were examined in the CASPT2 studies. Recently, Palmer *et al.*[32] reported a multireference double configuration interaction MRD-CI study, in which the intensity order of the valence $\pi-\pi^*$ excited states was $^1A_1(\text{middle})<^1B_2(\text{middle})<^1A_1(\text{very strong})<^1B_2(\text{strong})$. The order of these four excited states was the same in three bases (DZPR, TZVP, and QZVP), however, the oscillator strengths were different even qualitatively. In the latest experimental vacuum ultraviolet (VUV) spectroscopic study, a number of Rydberg transitions in the energy region of 6.0, 6.6, and 7.7–8.8 eV were observed, though they were discussed only briefly since the MRD-CI energies were too high to make a theoretical assignment, especially in the higher energy region. There are still some critical inconsistencies between the

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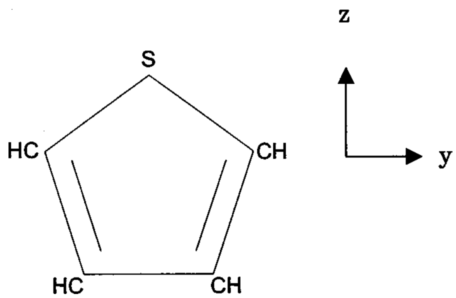

FIG. 1. Thiophene.

results of these two high-level *ab initio* studies. In particular, the calculated excitation energies and oscillator strengths for the second pair of valence π–π^* excited states ($^1A_1$ and $^1B_2$, corresponding to the most intense band in the VUV spectrum) were quite different between the CASPT2 and MRD-CI studies.

In this article, we study the electronic excitation spectrum of thiophene by the SAC-CI method as a series of our recent studies[38,39] on the five-membered ring compounds. There are two objectives in the present study: one is to reduce ambiguity in the assignment of the electronic spectrum of thiophene in a wide energy range, and the other is to give a theoretical basis for further experimental studies on thiophene. In Sec. II we outline the computational details. Calculated results and discussions are presented in Sec. III. A summary is given in Sec. IV.

II. COMPUTATIONAL DETAILS

All the calculations have been performed at the experimentally determined ground state geometry[40] with C_{2v} symmetry. The molecular plane used is on the yz-plane, and the C_2 axis on the z-axis as illustrated in Fig. 1. The calculated excitation energies are vertical in nature.

Dunning's augmented correlation consistent valence triple-zeta (AUG-cc-pVTZ)[41] basis set was used for S and C atoms though one f-function was removed from each C atom, and cc-pVTZ[42] was used for H atoms. Additionally, a set of diffuse Rydberg functions ($5s5p5d$) selected from the studies of Kaufmann *et al.*[43] was placed on the molecular center of the gravity to investigate the Rydberg states in a wide energy region. The total number of basis functions is 307. This type of augmented basis sets was used in the studies of Christiansen *et al.*[36,37] and in our recent calculations.[38,39] This set could describe widely different electronic structures of these five-membered ring compounds in the ground state, singlet, and triplet valence and Rydberg excited states with a high accuracy. The number of Hartree–Fock canonical orbitals, calculated by the GAUSSIAN98 package,[44] is 307, consisting of 22 occupied and 285 virtual orbitals. The self-consistent field (SCF) occupied valence orbitals and some important virtual orbitals are shown in Table I, together with their orbital energies, symmetries, and characters.

The details of the SAC/SAC-CI theory for calculating ground and excited states of molecules have been presented elsewhere,[45–51] and the calculations have been performed with the local module[51] of our laboratory. In all of the present SAC/SAC-CI calculations, the active space consists of 17 occupied orbitals and 285 virtual orbitals, only the $1s$ core molecular orbitals (MOs) being frozen. The detailed conditions of the SAC/SAC-CI calculations are exactly the same as those for cyclopentadiene,[38] furan, and pyrrole.[39]

TABLE I. Some important SCF occupied and unoccupied molecular orbitals (MOs).

MOs	Symmetry	Orbital energy (eV)	Nature
Occupied			
19	$2b_1$	−14.249	π
20	$6b_2$	−12.926	n(σ lone-pair orbital)
21 (next HOMO)	$3b_1$	−9.413	π_1
22 (HOMO)	$1a_2$	−8.916	π_2(node at sulfur)
Unoccupied			
23 (LUMO)	a_1	0.034	s-Rydberg
24	b_2	0.094	p_y-Rydberg
25	a_1	0.097	p_z-Rydberg
26	b_1	0.102	p_z-Rydberg
27	a_1	0.148	s-Rydberg
28	a_1	0.204	d_0-Rydberg
29	b_2	0.204	d_{-1}-Rydberg
30	a_2	0.210	d_{-2}-Rydberg
31	b_1	0.212	d_{+1}-Rydberg
32	a_1	0.212	d_{+2}-Rydberg
33	b_2	0.304	p_y-Rydberg
34	a_1	0.313	p_z-Rydberg
35	b_1	0.327	p_x-Rydberg
36	a_1	0.380	s-Rydberg
37	b_2	0.552	d_{-1}-Rydberg
38	a_1	0.553	d_0-Rydberg
39	a_2	0.571	d_{-2}-Rydberg
40	a_1	0.577	d_{+2}-Rydberg
41	b_1	0.578	d_{+1}-Rydberg
42	b_2	0.701	p_y-Rydberg
43	a_1	0.724	p_z-Rydberg
44	b_1	0.746	p_x-Rydberg
45	a_1	0.831	s-Rydberg
46	b_2	1.152	d_{-1}-Rydberg
47	a_1	1.162	d_0-Rydberg
48	a_2	1.214	d_{-2}-Rydberg
49	a_1	1.217	d_{+2}-Rydberg
50	b_1	1.230	d_{+1}-Rydberg
51	b_2	1.432	p_y-Rydberg
52	a_1	1.492	p_z-Rydberg
53	b_1	1.515	p_x-Rydberg
54	a_1	1.781	s-Rydberg
55	b_2	2.172	d_{-1}-Rydberg
56	a_1	2.224	d_0-Rydberg
57	a_1	2.337	d_{+2}-Rydberg
58	a_2	2.352	d_{-2}-Rydberg
59	b_1	2.390	d_{+1}-Rydberg
60	b_1	2.702	π_3^*
61	b_2	2.826	p_y-Rydberg
65	a_2	3.442	π_4^*
70	b_2	3.927	σ^*
72	b_1	4.219	σ^*
74	b_1	4.375	π_5^*
79	b_2	5.167	σ^*
82	a_2	5.649	π_6^*
84	b_2	6.438	σ^*
95	b_1	9.421	σ^*

TABLE II. Calculated singlet and triplet excitation energies ΔE (in eV), oscillator strengths $f(r)$, second moments and main configurations by SAC/SAC-CI method for thiophene.

State	Main configuration	SAC/SAC-CI		Second moment			
		ΔE (eV)	$f(r)$	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$	$\langle r^2\rangle$
Singlet							
$1\,^1A_1$	Ground state	0		31.1506	24.2497	27.0050	82.4052
$2\,^1A_1$	0.74(21-60)+0.34(21-74)−0.32(22-82)−0.24(22-65)	5.41	0.0911	31.7389	25.7192	27.3151	84.7732
$1\,^1A_2$	−0.50(22-45)+0.47(22-54)+0.43(22-36)	5.70	0.0000	48.0408	42.2990	41.6378	131.9777
$1\,^1B_2$	−0.84(22-60)−0.34(22-74)+0.23(22-59)	5.72	0.1131	32.2070	23.7881	29.7098	85.7050
$1\,^1B_1$	0.41(22-51)−0.35(22-42)−0.32(22-61)−0.28(22-70) −0.26(22-84)−0.26(22-79)	5.87	0.0112	34.8407	40.6329	35.8586	111.3322
$2\,^1A_2$	−0.38(21-70)−0.33(21-84)−0.32(21-79)+0.31(21-51) +0.31(21-55)−0.30(21-61)	6.03	0.0000	31.9277	34.1791	33.7306	99.8375
$2\,^1B_1$	0.50(21-45)−0.47(21-54)−0.43(21-36)−0.31(21-27)	6.12	0.0001	48.5316	42.0712	41.6709	132.2737
$3\,^1A_2$	0.53(22-43)−0.50(22-52)+0.42(22-34)−0.28(22-63)	6.41	0.0000	47.0079	38.1895	77.5094	162.7068
$2\,^1B_2$	0.55(22-44)−0.53(22-53)+0.41(22-35)−0.33(22-64)	6.41	0.0376	80.6863	35.5601	39.3059	155.5523
$3\,^1B_1$	−0.41(22-42)−0.35(22-33)−0.35(22-55)+0.35(22-70) +0.30(22-46)+0.30(22-51)	6.47	0.0165	43.5744	64.8495	46.8936	155.3175
$3\,^1A_1$	0.54(21-44)−0.52(21-53)+0.39(21-35)+0.33(21-64)	6.73	0.0655	77.8235	37.2392	36.4978	151.5604
$4\,^1A_2$	−0.50(22-57)−0.47(22-49)+0.31(22-40)+0.29(22-69)	6.73	0.0000	52.5661	43.2566	49.1488	144.9715
$4\,^1B_1$	−0.55(21-43)+0.51(21-52)−0.42(21-34)+0.28(21-63)	6.73	0.0193	46.1183	42.4244	75.9815	164.5242
$5\,^1A_2$	−0.52(22-47)+0.48(22-56)−0.39(22-38)−0.29(22-71)	6.75	0.0000	41.3948	53.8679	63.3268	158.5895
$6\,^1A_2$	0.48(21-42)+0.40(21-33)−0.35(21-51)−0.26(21-70)	6.89	0.0000	46.4728	79.0322	41.7282	167.2332
$4\,^1A_1$	−0.58(22-48)−0.56(22-39)+0.39(22-58)+0.28(22-30)	7.08	0.0177	91.7148	81.2631	42.2013	215.1792
$3\,^1B_2$	0.57(22-41)+0.56(22-50)−0.35(22-59)−0.30(22-31)	7.12	0.0033	96.1437	39.1037	89.8120	225.0594
$5\,^1B_1$	−0.46(21-57)−0.46(21-49)+0.33(21-40)+0.28(21-69)	7.14	0.0001	52.5975	36.0913	67.5834	156.2721
$6\,^1B_1$	0.51(22-37)+0.45(22-46)−0.28(22-29)+0.24(22-33)	7.15	0.0000	52.1380	94.2201	81.2187	227.5768
$7\,^1B_1$	−0.52(21-47)+0.44(21-56)−0.44(21-38)−0.25(21-71)	7.21	0.0000	46.2803	85.0816	46.0036	177.3655
$7\,^1A_2$	0.56(22-27)−0.47(22-23)−0.36(22-54)+0.22(22-36)	7.23	0.0000	151.6530	111.8982	92.8254	356.3766
$5\,^1A_1$	0.57(22-65)+0.46(22-82)+0.34(21-60)−0.20(21-59)	7.32	0.3614	48.5737	33.9397	36.3434	118.8568
$4\,^1B_2$	−0.54(21-65)−0.48(21-82)+0.25(22-26)+0.24(21-48)	7.40	0.1204	82.7311	48.9592	45.0122	176.7025
$5\,^1B_2$	0.43(22-26)−0.42(21-48)−0.41(21-39)−0.40(22-35)	7.43	0.0039	172.4345	89.4303	68.1378	330.0026
$8\,^1B_1$	0.62(22-24)−0.45(22-33)−0.36(22-51)−0.22(22-29)	7.45	0.0047	107.1687	252.7777	112.2372	472.1836
$8\,^1A_2$	0.62(22-25)−0.52(22-34)−0.36(22-52)−0.24(22-63)	7.46	0.0000	109.1968	94.4712	252.2310	455.8990
$6\,^1B_2$	0.38(21-65)+0.38(22-26)+0.35(21-39)+0.33(21-82) −0.32(22-35)+0.31(21-48)	7.46	0.0236	140.4010	73.7045	61.4728	275.5784
$6\,^1A_1$	−0.58(21-41)−0.55(21-50)+0.31(21-59)+0.29(21-31)	7.47	0.0336	96.5094	42.5028	87.3996	226.4118
$9\,^1A_2$	−0.48(22-32)+0.45(22-40)+0.29(22-28)−0.26(22-38)	7.54	0.0000	114.9392	75.1133	230.1971	420.2497
$10\,^1A_2$	0.60(22-28)−0.43(22-38)+0.28(22-32)−0.27(22-56)	7.59	0.0000	116.0788	231.7181	119.9996	467.7964
$9\,^1B_1$	0.55(21-27)−0.45(21-23)−0.36(21-54)+0.23(21-40)	7.61	0.0004	166.4129	107.4242	96.6257	370.4628
$10\,^1B_1$	−0.75(22-29)−0.31(22-46)+0.25(22-55)+0.20(22-37)	7.68	0.0001	109.9132	261.1500	247.5259	618.5892
$7\,^1B_2$	0.82(22-31)+0.35(22-50)−0.29(22-59)−0.13(22-41)	7.69	0.0020	293.3505	104.5606	286.1196	684.0307
$7\,^1A_1$	−0.80(22-30)−0.33(22-48)+0.32(22-58)+0.20(22-39)	7.70	0.0006	277.8417	261.4545	104.3382	643.6344
$8\,^1A_1$	0.63(21-26)−0.52(21-35)−0.36(21-53)−0.27(21-64)	7.79	0.0002	268.5184	106.1164	98.3973	473.0322
$11\,^1B_1$	−0.64(21-25)+0.48(21-34)+0.36(21-52)+0.23(21-63)	7.80	0.0072	110.5075	109.1804	267.9629	487.6508
$8\,^1B_2$	−0.71(22-26)−0.48(22-35)−0.28(22-44)−0.25(22-53)	7.85	0.0033	611.5824	210.3437	215.6045	1037.5305
$12\,^1B_1$	0.56(20-60)+0.34(21-32)−0.34(21-40)+0.27(20-74)	7.86	0.0004	96.5793	108.1910	140.5064	345.2767
$13\,^1B_1$	0.60(22-24)+0.51(22-33)+0.28(22-51)+0.19(22-42)	7.87	0.0035	202.0923	529.8150	224.2007	956.1080
$14\,^1B_1$	−0.49(21-32)−0.45(21-28)+0.33(21-40)+0.25(21-38)	7.95	0.0001	143.8030	266.6761	82.4519	492.9310
$9\,^1B_2$	−0.82(21-30)−0.35(21-48)+0.32(21-58)+0.17(21-39)	8.02	0.0001	288.0977	278.1591	105.9431	672.1999
$15\,^1B_1$	0.68(22-37)+0.46(22-29)+0.31(22-55)−0.19(22-62)	8.03	0.0000	143.7143	362.6991	351.5673	857.9807
$9\,^1A_1$	−0.59(21-31)−0.49(22-39)−0.31(22-30)−0.25(22-58)	8.06	0.0008	322.3675	220.6878	207.0026	750.0579
$10\,^1B_2$	−0.74(22-41)−0.40(22-31)−0.38(22-59)+0.23(22-50)	8.07	0.0007	365.0271	129.1955	355.0587	849.2814
$10\,^1A_1$	−0.56(21-31)+0.53(22-39)+0.32(22-30)+0.28(22-58)	8.08	0.0001	336.2777	244.0851	203.0907	783.4536
$11\,^1A_1$	−0.68(21-26)−0.50(21-35)−0.28(21-44)−0.27(21-53)	8.19	0.0004	595.9895	209.8464	207.3958	1013.2318
$11\,^1B_2$	0.73(22-44)−0.47(22-35)+0.32(22-64)+0.20(22-53)	8.20	0.0069	602.2870	207.4578	212.6442	1022.3890
$16\,^1B_1$	−0.67(22-42)+0.40(22-33)+0.37(22-62)−0.25(22-51)	8.21	0.0030	214.9969	527.3109	221.7682	964.0761
$17\,^1B_1$	0.63(21-25)+0.53(21-34)+0.29(21-52)+0.23(21-43)	8.22	0.0020	219.8853	224.5123	585.4795	1029.8772
$18\,^1B_1$	−0.60(21-32)−0.51(21-40)+0.25(21-23)+0.22(21-27)	8.30	0.0001	296.4145	275.6246	413.3376	985.3767
$19\,^1B_1$	−0.64(21-38)−0.53(21-28)−0.29(21-56)+0.19(21-71)	8.33	0.0006	153.0923	449.9668	292.1696	895.2287
$20\,^1B_1$	−0.54(22-62)+0.42(22-61)−0.34(21-27)+0.23(22-46)	8.38	0.0001	235.0066	217.8257	245.5606	698.3930
$12\,^1B_2$	−0.73(21-39)−0.42(21-30)−0.39(21-58)+0.21(21-48)	8.40	0.0000	371.9684	362.9376	132.7741	867.6801
$12\,^1A_1$	0.71(21-41)+0.45(21-31)+0.36(21-59)−0.22(21-50)	8.41	0.0003	379.6400	137.3506	368.4652	885.4558
$13\,^1A_1$	0.71(21-44)−0.48(21-35)+0.32(21-64)+0.20(21-53)	8.53	0.0018	606.5278	213.3733	211.1042	1031.0053
$14\,^1A_1$	−0.64(22-48)−0.53(22-58)+0.25(22-75)+0.21(19-60)	8.66	0.0001	241.0693	223.5991	95.5606	560.2290
$13\,^1B_2$	−0.66(22-50)−0.59(22-59)+0.25(22-81)+0.18(22-41)	8.70	0.0002	251.2184	90.4596	242.9286	584.6066
$15\,^1A_1$	−0.51(20-45)+0.46(20-54)+0.43(20-36)+0.31(20-27)	8.77	0.0426	58.4541	49.5909	43.8834	151.9285

TABLE II. (*Continued.*)

		SAC/SAC-CI		Second moment			
State	Main configuration	ΔE (eV)	$f(r)$	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle r^2 \rangle$
$14\ ^1B_2$	0.35(22-74)+0.33(22-64)−0.31(22-53)+0.28(20-51)	8.94	0.1281	108.5872	61.1085	62.1107	231.8064
$15\ ^1B_2$	0.57(22-64)−0.54(22-53)−0.20(22-74)−0.20(22-85)	9.02	0.0087	247.0414	97.8575	95.6634	440.5623
$16\ ^1B_2$	0.66(21-48)+0.58(21-58)−0.27(21-75)−0.18(21-39)	9.04	0.0023	249.1371	238.4051	92.2909	579.8332
$16\ ^1A_1$	0.62(21-50)+0.61(21-59)−0.21(21-81)+0.17(22-65)	9.07	0.0017	235.1688	88.8972	226.3588	550.4248
$17\ ^1B_2$	0.76(22-74)−0.30(22-60)−0.22(20-51)+0.20(20-42)	9.16	0.0225	53.7501	45.8525	47.4389	147.0415
$17\ ^1A_1$	0.37(21-64)+0.37(21-74)−0.34(21-53)+0.33(20-43)	9.30	0.0157	125.1763	60.0477	78.5895	263.8135
$18\ ^1A_1$	0.46(21-64)−0.42(21-53)−0.34(20-43)+0.33(20-52)	9.32	0.0162	164.4771	72.5581	87.8323	324.8675
$19\ ^1A_1$	−0.53(21-74)+0.34(22-82)−0.32(22-65)+0.32(21-60)	9.38	0.0211	105.4377	60.6730	56.8228	222.9334
$18\ ^1B_2$	0.84(22-72)+0.23(22-95)−0.22(22-81)−0.17(21-65)	9.44	0.0927	78.6144	36.1895	59.0746	173.8785
$20\ ^1A_1$	0.51(22-82)+0.46(21-74)−0.33(22-65)−0.28(19-60)	9.56	0.0390	74.5562	48.8127	48.8346	172.2035
$19\ ^1B_2$	0.53(21-65)−0.52(21-82)+0.35(20-42)+0.29(20-33)	9.68	0.0002	52.4212	63.3838	44.3538	160.1588
$21\ ^1A_1$	0.76(21-72)−0.27(21-74)+0.23(21-95)−0.19(21-81)	9.78	0.0319	75.6652	40.0539	57.4349	173.1540
$22\ ^1A_1$	−0.47(20-47)+0.41(20-56)−0.34(20-38)−0.25(21-72)	9.85	0.1378	52.7586	54.9992	74.1498	181.9075
Triplet							
$1\ ^3B_2$	0.81(22-60)+0.44(22-74)	3.94	⋯	31.1381	23.0524	28.6764	82.8668
$1\ ^3A_1$	0.78(21-60)+0.40(21-74)+0.27(22-82)	4.86	⋯	31.4461	25.8997	26.5303	83.8760
$1\ ^3A_2$	0.51(22-45)−0.48(22-54)−0.44(22-36)	5.75	⋯	49.6142	41.7454	43.4494	134.8091
$1\ ^3B_1$	0.43(22-51)−0.38(22-42)−0.32(22-61)	5.94	⋯	35.9006	43.7472	36.4166	116.0643

III. RESULTS AND DISCUSSION

We show some important SCF orbitals in Table I. The four occupied MOs in the highest occupied molecular orbital (HOMO) region are π- and lone-pair orbitals. In the unoccupied MOs, many Rydberg MOs appear first and the valence MOs appear in energy higher than 2.7 eV. The total SCF energy of thiophene is calculated to be −551.376 387 Hartree. The SAC ground-state energy is −551.667 755 Hartree, and the correlation energy is −0.291 368 Hartree.

The valence and Rydberg transitions are distinguished by the criteria discussed in our previous article[38] for the C_{2V} five-membered ring compounds. First, the A_2 and B_1 Rydberg states are not perturbed by the valence π–π^* transitions. Second, the second moment of the charge distribution $\langle r^2 \rangle$, and its components $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ give the size of the electron cloud of the state under consideration. In addition, the oscillator strength has also been used by some authors[30–32,34,35] as an indicator to distinguish valence with Rydberg states.

The Rydberg transitions originating from the $1a_2$ orbital (HOMO) are substantially different from those originating from the $3b_1$ orbital (next HOMO, see Table I), since the $1a_2$ orbital has a node at the sulfur atom. For convenience, they are labeled as R and R', respectively, in the present study.

The calculated excitation energies, oscillator strengths, main configurations, and second moments are shown in Table II. The calculated excitation energies which are used to assign the experimental data are shown in Table III, together with the other theoretical results by the CASPT2 and MRD-CI methods.

A. Energy range lower than 5 eV

The onset of the optical absorption in thiophene is located at 5 eV. Two lowest triplet transitions have been identified by the EEL[19–21] spectra at 3.8 and 4.7 eV, which are assigned to the $^3B_2$ and $^3A_1$ valence transitions, respectively. Our present calculations computed the $1\ ^3B_2$ state at 3.94 eV and the $1\ ^3A_1$ state at 4.86 eV. The present SAC-CI triplet excitation energies are in good agreement with experimental values. Calculated second moments of these two states are 82.9 a.u.^{2} and 83.9 a.u.^{2}, and these clearly characterize $1\ ^3B_2$ and $1\ ^3A_1$ as valence π–π^* excitations. The main configurations of $1\ ^3B_2$ are (22→60) and (22→74), and those of $1\ ^3A_1$ are (21→60), (21→74), and (22→82). CASPT2 gives the $1\ ^3B_2$ and $1\ ^3A_1$ states at 3.75 and 4.50 eV, respectively. MRD-CI gives the corresponding states at 4.45 and 5.03 eV, respectively. We also calculated two other triplet transitions, $1\ ^3A_2$ and $1\ ^3B_2$, at 5.75 and 5.94 eV, respectively. The corresponding states of CASPT2 calculations were given at 5.88 and 5.90 eV, respectively, which are close to the SAC-CI results.

B. Energy range 5–6.5 eV

The first VUV band (see Fig. 2, historically denoted as bands A and B) is located in this energy region. The fine structure on the rising side of band A was suggested to originate from the valence state with vibrational structures. Moreover, the MCD spectrum of thiophene shows two bands at 5.27 and 5.64 eV, respectively, with opposite signs in their B-values,[16–18] confirming the presence of two valence π–π^* excitations. Our present calculations support the above MCD experimental conclusion: we obtained the $2\ ^1A_1$ and $1\ ^1B_2$ states with the excitation energies computed at 5.41 and 5.72 eV with the oscillator strength 0.0911 and 0.1131, respectively, that are clearly responsible for the intensity of the first VUV band. The second moments ($\langle r^2 \rangle$) of the two states are 84.8 and 85.7 a.u.^{2}, respectively, which clearly define both of them as valence excited states comparing with that of the ground state ($\langle r^2 \rangle = 82.4$ a.u.). The main configurations of the $2\ ^1A_1$ state are π–π^* excitations of 21→60, 21→74, 22→82, and 22→65, etc., and those of the $1\ ^1B_2$ state are

TABLE III. SAC-CI results compared with the experimental excitation energies (in eV) and other theoretical results for thiophene.

		SAC/SAC-CI			CASPT2[b]		MRD-CI[c]		CI[d]	
State	Nature	$f(r)$	ΔE	Expt.[a]	ΔE	$f(r)$	ΔE	$f(r)$	ΔE	$f(r)$
$1\,^1A_1$	Ground state		0							
$2\,^1A_1$	Valence	0.0911	5.41	5.5	5.33	0.089	5.69[e]	0.119	6.67	0.068
$1\,^1A_2$	$3s$ Ryd.	forbidden	5.70	6.0	5.93	forbidden	5.779	forbidden		
$1\,^1B_2$	Valence	0.1131	5.72	5.5	5.72	0.070	6.00[e]	0.154	7.74	0.047
$1\,^1B_1$	$1a_2-\sigma^*$	0.0112	5.87	6.0			6.412			
$2\,^1A_2$	$3b_1-\sigma^*$	forbidden	6.03	6.0						
$2\,^1B_1$	$3s'$ Ryd.	0.0001	6.12	6.0	6.23	0.0002	6.334	0.000		
$3\,^1A_2$	$3p_z$ Ryd.	forbidden	6.41	6.606	6.58	forbidden	7.028	forbidden		
$2\,^1B_2$	$3p_x$ Ryd.	0.0376	6.41	6.606	6.56	0.0296	7.098	0.034		
$3\,^1B_1$	$3p_y$ Ryd.	0.0165	6.47	6.606	6.30	0.0303	6.387	0.000		
$3\,^1A_1$	$3p'_x$ Ryd.	0.0655	6.73	6.7–7.0	6.76	0.0150	7.311	0.021		
$4\,^1A_2$	$3d_{+2}$ Ryd.	forbidden	6.73		6.97	forbidden	7.594	forbidden		
$4\,^1B_1$	$3p'_z$ Ryd.	0.0193	6.73	6.7–7.0	6.83	0.0200	7.175	0.029		
$5\,^1A_2$	$3d_0$ Ryd.	forbidden	6.75		7.08	forbidden	7.853	forbidden		
$6\,^1A_2$	$3p'_y$ Ryd.	forbidden	6.89	6.7–7.0	6.35	forbidden				
$4\,^1A_1$	$3d_{-2}$ Ryd.	0.0177	7.08		7.23	0.0006	7.926	0.001		
$3\,^1B_2$	$3d_{+1}$ Ryd.	0.0033	7.12		7.28	0.0005	7.760	0.000		
$5\,^1B_1$	$3d'_{+2}$ Ryd.	0.0001	7.14		7.37	0.0011				
$6\,^1B_1$	$3d_{-1}$ Ryd.	0.0000	7.15		7.24	0.0010				
$7\,^1B_1$	$3d'_0$ Ryd.	0.0000	7.21		7.67	0.0001				
$7\,^1A_2$	$4s$ Ryd.	forbidden	7.23				7.624	forbidden		
$5\,^1A_1$	Valence	0.3614	7.32	7.05	6.69	0.185	7.91[e]	0.429	9.05	0.172
$4\,^1B_2$	Valence	0.1204	7.40	7.05	7.32	0.392	8.10[e]	0.131	9.81	0.486
$5\,^1B_2$	$4p_x/3d'_{-2}$ Ryd.	0.0039	7.43	7.786						
$8\,^1B_1$	$4P_y$ Ryd.	0.0047	7.45	7.786						
$8\,^1A_2$	$4P_z$ Ryd.	forbidden	7.46	7.786						
$6\,^1B_2$	$3d'_{-2}/4p_x$ Ryd.	0.0236	7.46		7.53	0.0022				
$6\,^1A_1$	$3d'_{+1}$ Ryd.	0.0336	7.47		7.57	0.0001				
$9\,^1A_2$	$4d_{+2}$ Ryd.	forbidden	7.54	8.006						
$10\,^1A_2$	$4d_0$ Ryd.	forbidden	7.59	8.006						
$9\,^1B_1$	$4s'$ Ryd.	0.0004	7.61	8.14						
$10\,^1B_1$	$4d_{-1}$ Ryd.	0.0001	7.68	8.006						
$7\,^1B_2$	$4d_{+1}$ Ryd.	0.0020	7.69	8.006						
$7\,^1A_1$	$4d_{-2}$ Ryd.	0.0006	7.70	8.006						
$8\,^1A_1$	$4p'_x$ Ryd.	0.0002	7.79	8.384						
$11\,^1B_1$	$4p'_z$ Ryd.	0.0072	7.80	8.384						
$8\,^1B_2$	$5p_x$ Ryd.	0.0033	7.85	8.221						
$12\,^1B_1$	$n-\pi^*/4d'_{+2}$ Ryd.	0.0004	7.86		7.77	0.0333				
$13\,^1B_1$	$5p_y$ Ryd.	0.0035	7.87	8.221						
$14\,^1B_1$	$4d'_{+2}$ Ryd.	0.0001	7.95	7.949						
$9\,^1B_2$	$4d'_{-2}$ Ryd.	0.0001	8.02	7.949						
$15\,^1B_1$	$5d_{-1}$ Ryd.	0.0000	8.03	8.317						
$9\,^1A_1$	$4d'_{+1}/5d_{-2}$ Ryd.	0.0008	8.06							
$10\,^1B_2$	$5d_{+1}$ Ryd.	0.0007	8.07	8.317						
$10\,^1A_1$	$4d'_{+1}/5d_{-2}$ Ryd.	0.0001	8.08							
$11\,^1A_1$	$5p'_x$ Ryd.	0.0004	8.19							
$11\,^1B_2$	$6p_x$ Ryd.	0.0069	8.20	8.436						
$16\,^1B_1$	$6p_y$ Ryd.	0.0030	8.21	8.436						
$17\,^1B_1$	$5p'_z$ Ryd.	0.0020	8.22							
$18\,^1B_1$	$5d'_{+2}/5s'$ Ryd.	0.0001	8.30							
$19\,^1B_1$	$4d'_0$ Ryd.	0.0006	8.33							
$20\,^1B_1$	$7p_y/5s'$ Ryd.	0.0001	8.38							
$12\,^1B_2$	$5d'_{-2}$ Ryd.	0.0000	8.40							
$12\,^1A_1$	$5d'_{+1}$ Ryd.	0.0003	8.41	8.559						
$13\,^1A_1$	$6p'_x$ Ryd.	0.0018	8.53							
$14\,^1A_1$	$6d_{-2}$ Ryd.	0.0001	8.66	8.486						
$13\,^1B_2$	$6d_{+1}$ Ryd.	0.0002	8.70	8.486						
$15\,^1A_1$	$n-s$ Ryd.	0.0426	8.77		9.10	0.0479				
$14\,^1B_2$	V./$7p_x$ Ryd.	0.1281	8.94							
$15\,^1B_2$	$7p_x$ Ryd./V.	0.0087	9.02							
$16\,^1B_2$	$6d'_{-2}$ Ryd.	0.0023	9.04							
$16\,^1A_1$	$6d'_{+1}$ Ryd.	0.0017	9.07							

TABLE III. (*Continued.*)

		SAC/SAC-CI			CASPT2[b]		MRD-CI[c]		CI[d]	
State	Nature	$f(r)$	ΔE	Expt.[a]	ΔE	$f(r)$	ΔE	$f(r)$	ΔE	$f(r)$
$17\,^1B_2$	V./$7p_y$ Ryd.	0.0225	9.16							
$17\,^1A_1$	V./$7p_x'$ Ryd.	0.0157	9.30							
$18\,^1A_1$	$7p_x'/n-p_z$ Ryd.	0.0162	9.32							
$19\,^1A_1$	$3b_1-\pi^*/1a_2-\pi^*$	0.0211	9.38							
$18\,^1B_2$	$\pi-\sigma^*$	0.0927	9.44							
$20\,^1A_1$	$1a_2-\pi^*/3b_1-\pi^*$	0.0390	9.56							
$19\,^1B_2$	$3b_1-\pi^*/n-P_y$	0.0002	9.68							
$21\,^1A_1$	$3b_1-\sigma^*$	0.0319	9.78							
$22\,^1A_1$	$n-d_0$ Ryd.	0.1378	9.85							
$1\,^3B_2$	Valence	⋯	3.94	3.8	3.75	⋯	4.45			
$1\,^3A_1$	Valence	⋯	4.86	4.7	4.50	⋯	5.03			
$1\,^3A_2$	$3s$ Ryd.	⋯	5.75		5.88	⋯		⋯		
$1\,^3B_1$	$3p_y$ Ryd	⋯	5.94		5.90	⋯		⋯		

[a]References 21–25, 32.
[b]Reference 29.
[c]Reference 32.
[d]Reference 12.
[e]Results calculated by TZVP basis set, see Ref. 32.

$\pi-\pi^*$ excitations of 22→60, 22→74, etc. Our present calculations suggest that band A is due to these two valence $\pi-\pi^*$ transitions and their vibrational structures. CASPT2 calculated the two states at 5.33 and 5.72 eV, respectively, and MRD-CI at 5.69 and 6.00 eV, respectively. Note that SAC-CI, CASPT2, and MRD-CI gave very similar theoretical results in this energy region.

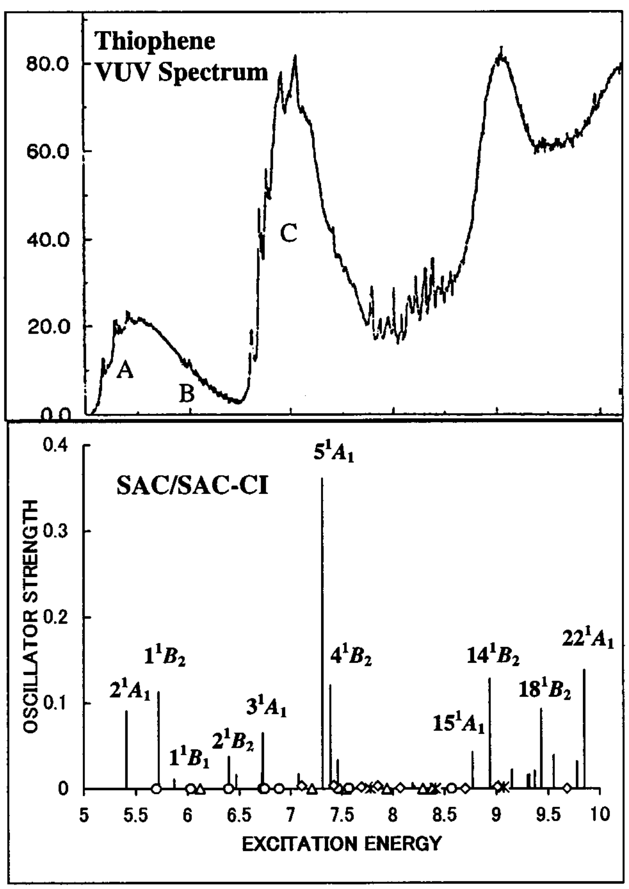

FIG. 2. VUV spectrum and SAC/SAC-CI theoretical spectrum of thiophene. ''*'' denotes singlet-excited state with A_1 symmetry, ''○'' denotes singlet-excited state with A_2 symmetry, ''△'' denotes singlet-excited state with B_1 symmetry, and ''◇'' denotes singlet-excited state with B_2 symmetry.

The weak fine structure around 6.0 eV (historically called band B) is absent in the condensed–phase spectra,[12–14] suggesting that this fine structure is Rydberg in nature. Palmer *et al.*[32] used the Rydberg equation to assign it to the $1a_2\rightarrow 3s$ Rydberg transition, though it is symmetry-forbidden. In our present calculations, the $1\,^1B_1$ state ($1a_2\rightarrow\sigma^*$ mixed with $1a_2\rightarrow 3p_y$ Rydberg) was calculated at 5.87 eV, the $2\,^1A_2$ state ($3b_1\rightarrow\sigma^*$ mixed with $3b_1\rightarrow 4d_{-1}$ Rydberg) at 6.03 eV, suggesting that valence $\pi\rightarrow\sigma^*$ transition is a main component of band B. In addition, the $3s$ and $3s'$ Rydberg transitions were also given in this energy region. The symmetry-forbidden $1\,^1A_2$ state ($1a_2\rightarrow 3s$) was given at 5.70 eV. The $2\,^1B_1$ state ($3b_1\rightarrow 3s$) was given at 6.12 eV, suggesting that this weak Rydberg transition might be included in the absorption of band B. Note that $1a_2\rightarrow\sigma^*$ and $1a_2\rightarrow\sigma^*$-type transitions are not mentioned in the CASPT2 study. MRD-CI calculated the corresponding states at 5.779 eV ($1a_2\rightarrow 3s$), 6.412 eV ($\pi Y+\sigma^*$), 6.852 eV ($\pi YZ+\sigma^*$), and 6.334 eV ($3b_1\rightarrow 3s$), respectively.

C. Energy range 6.5–7.7 eV

The second VUV band (historically called band C) is located in this region, and the maximum of the band is around 7.05 eV. The fine structure on the rising side of C band (around 6.6 eV) was suggested to associate with $3p$ Rydberg transitions.[5,32] Most of the intensity in this band was assumed to originate from the excitations of the further valence $\pi-\pi^*$ character.[5,32] Our present calculations strongly support this assignment.

The $3\,^1A_2$ ($1a_2\rightarrow 3p_z$ Rydberg), $2\,^1B_2$ ($1a_2\rightarrow 3p_x$ Rydberg), and $3\,^1B_1$ ($1a_2\rightarrow 3p_y$ Rydberg) states were calculated at 6.41, 6.41, and 6.47 eV, respectively. We assign this $3p$ series of Rydberg states to the peak of 6.606 eV since our

TABLE IV. Excitation energies (in eV) and oscillator strengths calculated by the SAC-CI method for the valence excitations of cyclopentadiene (CP), furan, pyrrole, and thiophene.

	CP		Furan		Pyrrole		Thiophene	
State	ΔE	$f(r)$	ΔE	$f(r)$	ΔE	$f(r)$	ΔE	$f(r)$
$1\,^1B_2$	5.54	0.1305	6.40	0.1852	6.48[a]	0.0475	5.72	0.1131
$2\,^1A_1$	6.76	0.0009	6.79	0.0000	6.41	0.0002	5.41	0.0911
$^1A_1$	8.17	0.5377	8.34	0.4826	7.88	0.3252	7.32	0.3614
$^1B_2$	⋯	⋯	9.08	0.1662	8.25	0.2553	7.40	0.1204
$^3B_2$	3.40	0.0	4.39	0.0	4.58	0.0	3.94	0.0
$^3A_1$	5.18	0.0	5.63	0.0	5.08	0.0	4.86	0.0

[a]This state ($2\,^1B_2$) was strongly mixed with Rydberg $3p$ transitions, see Ref. 39.

calculated excitation energies of several lowest Rydberg states are systematically lower than the experimental data, which also occurred in our previous studies for cyclopentadiene, furan, and pyrrole. The $3p'$ Rydberg series were given at 6.73 eV ($3\,^1A_1, 3b_1 \rightarrow 3p_x$), 6.73 eV ($4\,^1B_1, 3b_1 \rightarrow 3p_z$), and 6.89 eV ($6\,^1A_2, 3b_1 \rightarrow 3p_y$). From our present calculations these $3p'$ Rydberg transitions might also be responsible for the fine structure of the rising side of C band (up to 7.05 eV). Derrick *et al.*[5] supposed that the first four peaks of C band are due to *p*-type Rydberg excitations. In agreement with this assignment, Palmer *et al.*[32] assigned the peak at 6.606 eV to the $1a_2 - 3p$ Rydberg transitions. Our present calculations support these general experimental assignments.

Our present calculations gave the $5\,^1A_1$ state at 7.32 eV with oscillator strength 0.3614, and the $4\,^1B_2$ state at 7.40 eV with oscillator strength 0.1204, which are the main components of band C. The nature of the $5\,^1A_1$ state is a mixture of the $\pi \rightarrow \pi^*$ transitions ($22 \rightarrow 65$) and ($22 \rightarrow 82$) with ($21 \rightarrow 60$). The second moment is 118.9 a.u.^{2}, a little lager than that of the ground state (82.4 a.u.^{2}). The nature of $4\,^1B_2$ state is of strong mixture of $\pi \rightarrow \pi^*$ transitions ($21 \rightarrow 65$) and ($21 \rightarrow 82$) with Rydberg transitions ($22 \rightarrow 26$) and ($21 \rightarrow 48$), and this mixture is responsible for the large second moment (176.7 a.u.^{2}) of this state. We conclude that a significant portion of the electronic absorption intensity of C band is due to these two valence $\pi \rightarrow \pi^*$ excitations ($5\,^1A_1$ and $4\,^1B_2$) above-mentioned, especially due to the $5\,^1A_1$ valence $\pi \rightarrow \pi^*$ transition. Table IV shows clearly that this assignment agrees with the general trend of the most intense absorption band of the other five-membered ring compounds.[38,39] MRD-CI gave the similar trend of oscillator strengths for these two valence $\pi \rightarrow \pi^*$ transitions, though the excitation energies in the MRD-CI study were overestimated.

Note that CASPT2 gave the corresponding valence $\pi \rightarrow \pi^*$ excitations of the $3\,^1A_1$ state at 6.69 eV with the oscillator strength of 0.1850 obtained by CASSCF state interaction (CASSI) method, and the $4\,^1B_2$ state at 7.32 eV with CASSI oscillator strength of 0.3923. The relative intensities of these two states are calculated oppositely by CASSI to those by SAC-CI and MRD-CI methods. It deserves to be pointed out that a further polarization experimental study, e.g., magnetic circle dichroism study, on the band C is crucial in the future to verify the relative intensities of the $5\,^1A_1$ and $4\,^1B_2$ states assigned to C band.

On the higher energy shoulder of C band, our present calculations gave $3d$ and $3d'$ Rydberg transitions (see Table III for detailed numerical results). There are no experimental assignments in this energy region, but we propose the existence of the Rydberg states in this energy region of the spectrum.

D. Energy range 7.7–10 eV

The fine structure in 7.7∼8.8 eV is suggested by the present calculations to represent the Rydberg excitations. Most of them are identified to the two Rydberg series converging to IP_1 ($1a_2$, 8.872 eV) and IP_2 ($3b_1$, 9.52 eV), respectively. In order to calculate Rydberg states in this region as accurate as possible we use the molecule-centered diffuse functions ($5s5p5d$) in the present calculations. The $4p$, $4d$, $4s'$, $4p'$, $5p$, $4d'$, $6p$, $5d'$, and $6d$ Rydberg series are computed in this energy region, and the excitation energies and the natures of electronic states are shown in Table III. Since it is the first time to make a theoretical assignment in this far ultraviolet region, there may be room left for some variation in future theoretical and experimental studies.

Palmer *et al.*[32] experimentally assigned the absorption at 7.786 eV to $4p$ Rydberg series, absorption at 7.949 eV to $3d'$ Rydberg, absorption at 8.006 eV to $4d$ Rydberg series, absorptions at 8.14–8.16 eV to $4s'$ Rydberg series, absorption at 8.221 eV to $5p$ Rydberg series, absorption at 8.317 eV to $5d$ Rydberg series, absorption at 8.384 eV to $4p'$ Rydberg series, absorption at 8.436 eV to $6p$ Rydberg series, and absorption at 8.486 eV to $6d$ Rydberg series. Note that this experimental assignment itself was unable to specify, for example, p_x, p_y, and p_z Rydberg states. Our present calculations confirm that most of the Rydberg states above-mentioned are located at this energy region, and support most of the experimental assignments except for the $3d'$ Rydberg assignment. Our results, as discussed in 6.5–7.7 eV energy region, gave $3d'$ Rydberg series at 7.14–7.47 eV. It is reasonable to assign the absorption 7.949 eV to the $4d'$ Rydberg series, which were computed at 7.86–8.08 eV energy region. We made a comparison between our theoretical assignments and experimental assignments in Table III. We expect that the present results will stimulate new experimental and theoretical studies on the electronic states in this far ultraviolet region.

The excitation of the lone pair electron on the sulfur

TABLE V. Molecular orbital energies (in eV) and the main configurations of the lowest $^1A_1$ valence π–π^* excited states of cyclopentadiene, furan, pyrrole, and thiophene.

		Cyclopentadiene	Furan	Pyrrole	Thiophene
Main Configuration		$0.54(\pi_1\rightarrow\pi_3^*)$	$0.58(\pi_1\rightarrow\pi_3^*)$	$-0.58(\pi_1\rightarrow\pi_3^*)$	$0.74(\pi_1\rightarrow\pi_3^*)$
		$+0.49(\pi_2\rightarrow\pi_4^*)$	$+0.47(\pi_2\rightarrow\pi_4^*)$	$+0.47(\pi_2\rightarrow\pi_4^*)$	$-0.24(\pi_2\rightarrow\pi_4^*)$
		$-0.39(\pi_2\rightarrow\pi_6^*)$	$-0.43(\pi_2\rightarrow\pi_6^*)$	$-0.40(\pi_2\rightarrow\pi_6^*)$[a]	$-0.32(\pi_2\rightarrow\pi_6^*)$
		$-0.15(\pi_1\rightarrow\pi_5^*)$	$+0.24(\pi_1\rightarrow\pi_5^*)$	$-0.26(\pi_1\rightarrow\pi_5^*)$	$+0.34(\pi_1\rightarrow\pi_5^*)$
Orbital Energy (eV)	π_1	−11.244 (17th)	−10.835 (17th)	−9.454 (17th)	−9.413 (21st)
	π_2	−8.368 (18th)	−8.702 (18th)	−8.054 (18th)	−8.916 (22nd)
	π_3^*	2.938 (48th)	3.439 (48th)	3.787 (52nd)	2.702 (60th)
	π_4^*	4.095 (54th)	4.043 (53rd)	4.145 (53rd)	3.442 (65th)
	π_5^*	5.014 (60th)	6.298 (61st)	6.465 (62nd)	4.375 (74th)
	π_6^*	7.362 (67th)	6.988 (64th)	7.254 (66th)	5.649 (82nd)
Difference of (eV)	$\pi_3^*-\pi_1$	14.182	14.274	13.241	12.115
	$\pi_4^*-\pi_2$	12.463	12.745	12.199	12.358
	$\pi_6^*-\pi_2$	15.730	15.690	15.308	14.565
	$\pi_5^*-\pi_1$	16.258	17.133	15.919	13.788

[a]The sign of coefficients of the SCF 66th molecular orbital in pyrrole is opposite to those of the corresponding orbitals in other molecules.

atom to the π^* orbitals have high energy, as expected, but no experimental evidence is available: it has been suggested that the corresponding peak is covered by the π–π^* bands. The lowest $n-\pi^*$ state, $12\,^1B_1$, is predicted at 7.86 eV in the present calculations. CASPT2 also calculated the corresponding state at 7.77 eV.

In the higher energy region of 8.8–10 eV, it seems difficult to give a confirmed interpretation since IP_1 and IP_2 are also located in this region. Our present calculations give some higher valence excitations, π–π^* and π–σ^*, etc. in this region, which are more or less influenced by the higher Rydberg states. The detailed results are shown in Tables II and III.

E. Comparison with other five-membered ring compounds

In Table IV, we make a comparison of the valence singlet and triplet excited states of thiophene with those of cyclopentadiene, furan, and pyrrole for which similar studies have been carried out. Table IV shows that the $2\,^1A_1$ state is the lowest singlet excited state in thiophene and its oscillator strength is relatively strong only in thiophene. Therefore, only in thiophene, the $2\,^1A_1$ state has been clearly identified by experiments. A good agreement of the theoretical excitation energy and oscillator strength with the experimental ones in the case of thiophene gives an indirect support to our previous assignment of the $2\,^1A_1$ state in the other five-membered ring compounds.[38,39]

Here we qualitatively interpret the different trend of the $2\,^1A_1$ states between thiophene and other five-membered ring compounds. To simplify the analysis we assume that the excitation energy of the $2\,^1A_1$ state is approximately related to the orbital energy differences in the main configurations. The main configurations of the $2\,^1A_1$ states of cyclopentadiene, furan, pyrrole, and thiophene are listed in Table V, together with the orbital energies of the relevant MOs and their differences. In thiophene, π_1 is relatively unstable due to the antibonding nature between π_1 and $3p_z$ of sulfur, while π_3^* becomes stable due to the $3p_z$ bonding nature. Therefore, the orbital energy difference $\Delta E(\pi_3^*-\pi_1)$ becomes smaller and the $2\,^1A_1$ transition is dominated by $\pi_1\rightarrow\pi_3^*(0.74)$ only in thiophene. For this reason, in thiophene, the excitation energy of the $2\,^1A_1$ state becomes lowest, comparing with the same states of cyclopentadiene, furan, and pyrrole.

Furthermore, from Table V we see that the main configurations of the $2\,^1A_1$ states of cyclopentadiene, furan, and pyrrole are very similar, and therefore, it is easy to understand that the oscillator strengths of the $2\,^1A_1$ states in these three molecules are similar in magnitude. In thiophene, however, the $2\,^1A_1$ state is dominated by different main configurations and the weight of configuration $\pi_1\rightarrow\pi_3^*(0.74)$ is much larger than those in the other three molecules (0.54–0.58). This obvious difference gives rise to a larger contribution of the configuration $(\pi_1\rightarrow\pi_3^*)$ to the transition dipole moment of the $2\,^1A_1$ state in thiophene.

Note that the CASPT2 (Ref. 29) study showed that the $2\,^1A_1$ state of thiophene has the smallest weight of the doubly excited configurations among these molecules of interest. In the cases of cyclopentadiene, furan, and pyrrole, the contributions of the doubly excited configurations to the $2\,^1A_1$ state were large. In SAC-CI calculations, however, the contributions of doubly excited configurations to the $2\,^1A_1$ states are small in all four molecules. Nevertheless, both SAC-CI and CASPT2 methods give similar results on the $2\,^1A_1$ state of thiophene.

IV. CONCLUSIONS

An extended investigation of the electronic excitation spectra of thiophene has been carried out by the SAC/SAC-CI method. To give a satisfactory theoretical interpretation of the VUV and EEL spectra of thiophene, the 70 singlet and four lowest triplet electronic states were computed. The calculated triplet valence $\pi\rightarrow\pi^*$ excited states $1\,^3B_2$ (3.94 eV) and $1\,^3A_1$ (4.86 eV) agree well with the EEL spectroscopic data. Two pairs of singlet valence $\pi\rightarrow\pi^*$ excitations were given, which span the general profile of the VUV spectrum lower than 7.7 eV. The $2\,^1A_1$ (5.41 eV) and

$1\,^1B_2$ (5.72 eV) states were assigned to cause most of the intensity of the first band of the VUV spectrum. The $5\,^1A_1$ (7.32 eV) and $4\,^1B_2$ (7.40 eV) states were assigned to constitute most of the second band of the VUV spectrum. Our present results suggest that the intensity of the second band, i.e., C band, is largely due to the $5\,^1A_1$ valence $\pi\rightarrow\pi^*$ excited state (see Fig. 2), instead of due to the $4\,^1B_2$ valence $\pi\rightarrow\pi^*$ excited state suggested by the CASPT2 study. Polarization experiment on the C band is, therefore, very interesting. In addition, a number of Rydberg states in the energy region of 6.0, 6.6, and 7.7–8.8 eV was assigned according to our present calculations. This study gives the first theoretical assignment in the far ultraviolet region (7.7–8.8 eV) of the spectrum and is expected to provide a theoretical basis for further experimental and theoretical studies on the excited states of thiophene in this energy region.

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[1] W. C. Price and A. D. Walsh, Proc. R. Soc. London, Ser. A **179**, 201 (1941).
[2] L. W. Pickett, N. J. Hoeflich, and T.-C. Liu, J. Am. Chem. Soc. **73**, 4865 (1951).
[3] P. A. Mullen and M. K. Orloff, J. Chem. Phys. **51**, 2276 (1969).
[4] J. H. D. Eland, Int. J. Mass Spectrom. Ion Phys. **2**, 471 (1969).
[5] P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, Int. J. Mass Spectrom. Ion Phys. **6**, 161 (1971).
[6] P. J. Derrick, L. Asbrink, O. Edqvist, and E. Lindholm, Spectrochim. Acta, A **27**, 2525 (1971).
[7] M. Bavia, F. Bertinelli, C. Taliani, and C. Zauli, Mol. Phys. **31**, 479 (1976).
[8] C. D. Cooper, A. D. Williamson, J. C. Miller, and R. N. Compton, J. Chem. Phys. **73**, 1527 (1980).
[9] J. L. Roebber, D. P. Gerrity, R. Hemley, and V. Vaida, Chem. Phys. Lett. **75**, 104 (1980).
[10] L. Nyulaszi, J. Mol. Struct. **273**, 133 (1992).
[11] M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Acadamic, New York, 1975), Vol. II.
[12] G. L. Bendazoli, F. Bertineli, P. Palmieri, A. Brillante, and C. Taliani, J. Chem. Phys. **69**, 5077 (1978).
[13] L. Nyilaszi and T. Veszpremi, J. Mol. Struct. **140**, 253 (1986).
[14] L. Nyilaszi and T. Veszpremi, J. Mol. Struct. **140**, 353 (1986).
[15] L. Nyilaszi and T. Veszpremi, Chem. Scr. **28**, 331 (1988).
[16] R. Hakansson, B. Norden, and E. W. Thulstrup, Chem. Phys. Lett. **50**, 305 (1977).
[17] B. Norden, R. Hakansson, P. B. Pedersen, and E. W. Thulstrup, Chem. Phys. **33**, 355 (1978).
[18] N. Igarashi, A. Tajiri, and M. Hatano, Bull. Chem. Soc. Jpn. **54**, 1511 (1981).
[19] W. M. Flicker, O. A. Mosher, and A. Kuppermann, J. Chem. Phys. **64**, 1315 (1976).
[20] W. M. Flicker, O. A. Mosher, and A. Kuppermann, Chem. Phys. Lett. **38**, 489 (1976).
[21] E. H. Van Veen, Chem. Phys. Lett. **41**, 535 (1976).
[22] K. Tanaka, T. Nomura, T. Noro, H. Tatewaki, T. Takada, H. Kashiwagi, F. Sasaki, and K. Ohno, J. Chem. Phys. **67**, 5738 (1977).
[23] W. Butscher and K.-H. Thunemann, Chem. Phys. Lett. **57**, 224 (1978).
[24] K.-H. Thunemann, R. J. Buenker, and W. Butscher, J. Chem. Phys. **47**, 313 (1980).
[25] D. C. Rawlings and E. R. Davidson, Chem. Phys. Lett. **98**, 424 (1983).
[26] D. C. Rawlings, E. R. Davidson, and M. Gouterman, Int. J. Quantum Chem. **26**, 237 (1984).
[27] H. Nakatsuji, O. Kitao, and T. Yonezawa, J. Chem. Phys. **83**, 723 (1985).
[28] L. Serrano-Andres, M. Merchan, I. Nebot-Gil, B. O. Roos, and M. Fulscher, J. Am. Chem. Soc. **115**, 6184 (1993).
[29] L. Serrano-Andres, M. Merchan, M. Fulscher, and B. O. Roos, Chem. Phys. Lett. **211**, 125 (1993).
[30] M. H. Palmer, I. C. Walker, C. C. Ballard, and M. F. Guest, Chem. Phys. **192**, 111 (1995).
[31] M. H. Palmer, I. C. Walker, and M. F. Guest, Chem. Phys. **238**, 179 (1998).
[32] M. H. Palmer, I. C. Walker, and M. F. Guest, Chem. Phys. **241**, 275 (1999).
[33] H. Nakano, T. Tsuneda, T. Hashimoto, and K. Hirao, J. Chem. Phys. **104**, 2312 (1996).
[34] A. B. Trofimov and J. Schirmer, Chem. Phys. **214**, 153 (1997).
[35] A. B. Trofimov and J. Schirmer, Chem. Phys. **224**, 175 (1997).
[36] O. Christiansen and P. Jørgensen, J. Am. Chem. Soc. **120**, 3423 (1998).
[37] O. Christiansen, J. Gauss, J. Stanton, and P. Jørgensen, J. Chem. Phys. **111**, 525 (1999).
[38] J. Wan, M. Ehara, M. Hada, and H. Nakatsuji, J. Chem. Phys. **113**, 5245 (2000).
[39] J. Wan, J. Meller, M. Hada, M. Ehara, and H. Nakatsuji, J. Chem. Phys. **113**, 7853 (2000).
[40] J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *LANDOLT-BORNSTEIN, Numerical Data and Functional Relationships in Science and Technology*, New Series, Group II: Atomic and Molecular Physics, Structure Data of Free Polyatomic Molecules (Springer-Verlag, Berlin-Heidelberg, 1976), Vol. 7.
[41] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[42] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[43] K. Kaufmann, W. Baumeister, and M. Jungen, J. Phys. B **22**, 2223 (1989).
[44] GAUSSIAN 98, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.*, Gaussian, Inc., Pittsburgh, PA, 1998.
[45] H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978).
[46] H. Nakatsuji, Chem. Phys. Lett. **59**, 362 (1978).
[47] H. Nakatsuji, Chem. Phys. Lett. **67**, 329 (1979).
[48] H. Nakatsuji, *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski (World Scientific, Singapore, 1997), Vol. 2.
[49] H. Nakatsuji, Acta Chim. Hung. **129**, 719 (1992).
[50] H. Nakatsuji, Chem. Phys. **75**, 425 (1983).
[51] H. Nakatsuji, M. Hada, M. Ehara, J. Hasegawa, T. Nakajima, H. Nakai, O. Kitao, and K. Toyota, SAC/SAC-CI program system (SAC-CI96) for calculating ground, excited, ionized, and electron attached states and singlet to septet spin multiplicities.